

# **Carbon and nitrogen isotopic ratio of the water-insoluble fraction in air filter particulate matter**

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## Introduction

Our objective in this study was to get from the filter samples as many isotopic data as possible for the source apportionment study. At first bulk EA-IRMS measurement was done, and the data clearly indicate the source of particulate matter (PM), but we could not explain the high nitrogen delta values measured in "Poly" samples. After one year cooled storage of the samples, the EA-IRMS measurement was repeated and water extraction was applied. We did not analyze the water fraction in this study.

According to literature the inorganic [1-3] water-soluble nitrogen compounds in air PM<sub>10</sub> are mainly ammonium nitrate and ammonium nitrite [2-5]. Contribution of organic nitrogen (ON) to total dissolved nitrogen particles is significant, in the range ~ 20 - 65 % [6]. There is no major group of components in the ON fraction [1, 7-11], as an example urea or amino acid can be mentioned. The water dissolved organic nitrogen can be analysed separately in EA-IRMS and the procedure how to perform such measurement is published by Kelly et al. [12].

Total carbonaceous aerosol comprises a complex mixture, which is classified mainly in two fractions: elemental carbon (EC, also called black carbon or soot) and organic carbon (OC). EC is emitted directly from combustion sources and undergoes little chemical transformation. It is a good indicator of primary anthropogenic air pollutants. However, OC can originate both from primary emission sources and from chemical reactions of gaseous organic precursor in the atmosphere [13]. In most urban areas OC and EC contribute ~ 20 to 50 % of fine particle mass [14].

The molecular composition of the fine particulate organics remains poorly characterized because these particles contain hundreds of organic compounds that cover a wide range of carbon numbers, functional groups and solubility in extraction media. Only about 10 % of the organic mass has been attributed to specific compounds. In prior experimental studies conducted in urban and non-urban locations in the continental U.S. and Japan, a substantial fraction (one-fifth to two-thirds) of the total particulate carbon (OC and EC) was found to be water-soluble organic carbon (WSOC) [15].

In this report the water-soluble and water-insoluble fractions were separated. The carbon and nitrogen isotopic ratios were measured in the water-insoluble fraction. To check the stability of the nitrogen isotopic ratio (expressed as  $\delta^{15}\text{N}_{\text{AIR}}$ ) and the carbon isotopic ratio (expressed as  $\delta^{13}\text{C}_{\text{VPDB}}$ ) the bulk EA analysis was repeated for some sources and ambient air samples.

## Experimental

### 1. Water extraction

Prior to analysis, all samples were extracted into aqueous solution. The ambient air filter samples were divided into small pieces (approximately 8 pieces of 1 cm<sup>2</sup> for each sample) in the case of source samples two-thirds of the circular filter samples (diameter 2 cm) was used for the water extraction. The sample pieces were cut so that they fell directly into a clean, labelled 5 ml centrifuge tube. The centrifuge tubes were filled with of Milli-Q<sup>TM</sup> water. After capping each tube was shaken gently so as to ensure that all pieces were moving freely within the water and none were stuck to its side. The tubes were placed in an ultra-sonic bath for 1 h, after which the extracts were centrifuged for 15 min. The water extracts were decanted and the centrifuge tubes were put into the oven and dried 12 h at 55 °C.

## 2. Carbon and nitrogen EA-IRMS measurement

The method used was Elemental Analysis – Isotope Ratio Mass Spectrometry. This is the common method for the measurement of nitrogen and carbon stable isotopes in solid bulk materials. The instrument used was an EA-Delta<sup>plus</sup> from Thermo.

In general, in a small (0.4 ml) tin foil capsule, between 0.1 and 1 mg of the substance under analysis is weighed. In this application approximately one cm<sup>2</sup> of quartz filter containing the PM10 sample was weighed and put into the capsule. Sample weight including filter material was 10 mg. The capsule is folded to hold the substance. The capsules are loaded into the autosampler. From here the online continuous flow analysis is starting. In short, for one individual analysis, the sample capsule is dropped by the autosampler into a column at 1025 °C containing an oxidant material, Cr<sub>2</sub>O<sub>3</sub>. Under a constant flow of helium, O<sub>2</sub> is added to ensure complete oxidation to CO<sub>2</sub> and NO<sub>x</sub> of the sample substance. These gases are transported in the stream of He towards a second column, which contains Cu at 650 °C. This will reduce the nitrogen oxides NO<sub>x</sub> to nitrogen gas N<sub>2</sub>. Further transport in He over a column of Mg(ClO<sub>4</sub>)<sub>2</sub> will remove the water, which was formed in the oxidative process. The gasses then pass over a short packed (molsieve) gas chromatographic column, which will ensure separation of the different gasses before they arrive through an open split coupling (Conflo II) in the isotope ratio mass spectrometer. The IRMS will measure the different ions from different isotopic composition of a gas (CO<sub>2</sub> for carbon, N<sub>2</sub> for nitrogen) on 3 or 2 fixed faraday cup detectors.

All measurements are done in comparison to a working reference, since IRMS is a differential system. The working references are gasses injected in the Conflo II open split interface through capillaries.

For carbon this is CO<sub>2</sub> from a gas bottle and for nitrogen this is N<sub>2</sub> from a gas bottle. Both are in their turn measured, using the same equipment, versus an internationally agreed reference material, with a given  $\delta$  value in per mill. References used were NBS19 and L-SVEC for carbon and USGS 32 and IAEA-N1 for nitrogen. During measurement the delta values of reference gases (N<sub>2</sub> and CO<sub>2</sub>) were constantly checked, after each five filter samples, our internal reference standard - methionine was measured.

In 2006 a total of 86 samples was analysed including 24 source samples, which represents 14 different sources. After one year of cooled storage (4 °C) the bulk measurement was repeated for 15 source samples and 3 ambient air samples. The water-insoluble fraction was measured in 23 source samples and in five ambient air samples. In all cases we analyzed the PM with filter material; this is correct since the blank filter measurement does not show the presence of carbon or nitrogen.

## **Results and discussion**

The filter samples were measured before and after water extraction; all isotopic data are presented in Table 1. Figures 1-4 show the comparison of the isotopic results obtained in the same filter samples in 2006 and 2007.

Figure 1 presents results obtained in 2006. We see that Zakopane samples can be linked to residential coal and/or wood burning. Other samples, specifically the "Poly" samples show quite high  $\delta^{15}\text{N}_{\text{Air}}$  values. It is likely that one or more sources with high  $\delta^{15}\text{N}_{\text{Air}}$  values are not represented in this study. Fractionation, i.e. altering  $\delta^{15}\text{N}_{\text{Air}}$  value in the sampling process or after sampling could also explain the high values found in the samples. The fact that this has not happened in the Zakopane samples does not support that hypothesis.

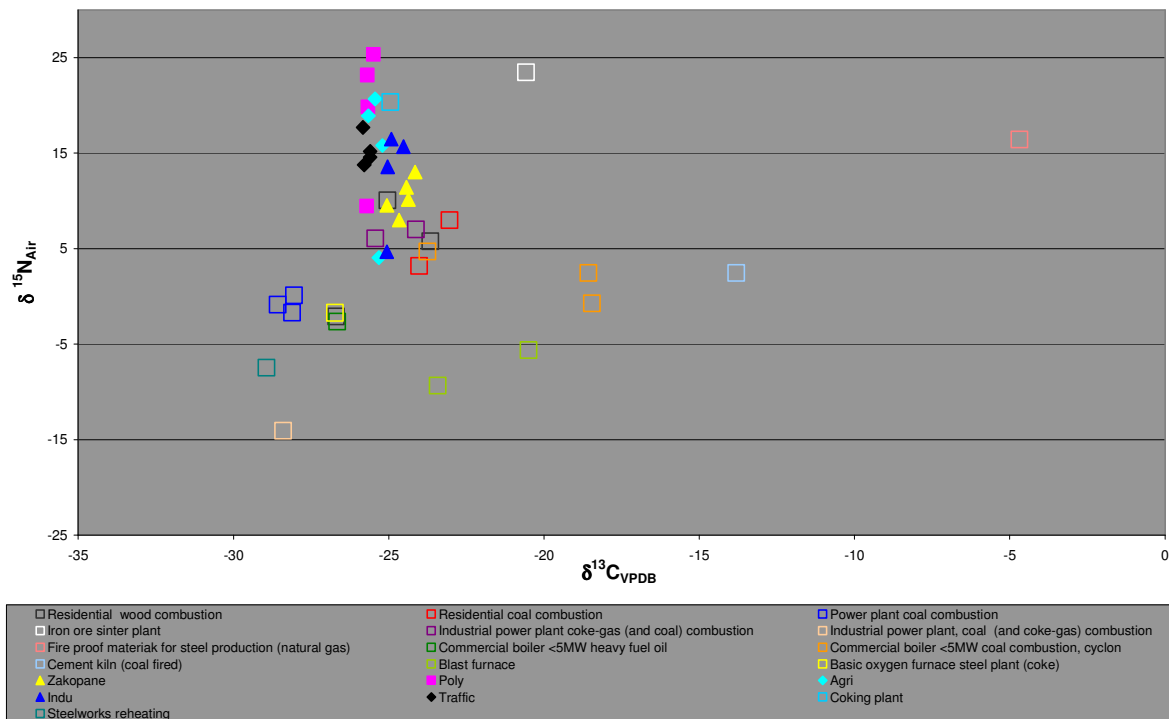


Figure 1. Carbon and nitrogen isotopic composition of the source and ambient air samples (Zakopane, Poly, Agri, Indu, Traffic) measured in April 2006.

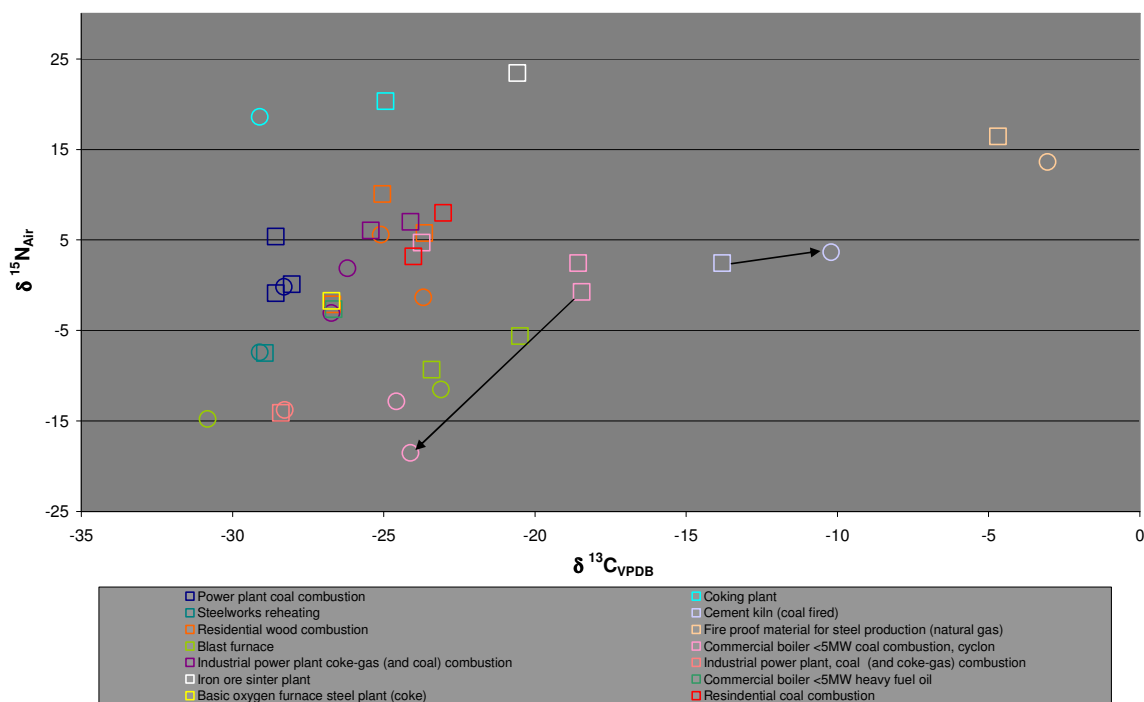


Figure 2. Comparison of C and N isotopic values for source samples measured in 2006 – square symbols and repeated in 2007 – circle symbols; arrows indicate apparent fractionation

Figure 2 shows the changes of the carbon and nitrogen isotopic ratio after 1 year cooled storage. The bulk measurement was repeated for 15 source and 3 ambient air samples (Table 1). Only for two sources (steelworks reheating and industrial power plant coal (+ coke-gas)) the isotopic data were close to those obtained in 2006. For nitrogen and carbon isotopes the changes were in the range of 1 to 20 ‰ and 0.5 to 7 ‰ respectively. There is no indication in these data of any systematic depletion or enrichment of any of the isotopes between the analysis done in 2006 and in 2007.

These changes in isotopic composition can be explained by two hypotheses. Firstly, the storage conditions were not suitable with a possibly too high temperature. However, the ambient air samples, stored in identical conditions, do not show differences in carbon or nitrogen isotopic composition. Secondly, and more likely, some reactions on the sample filters, already initiated in the PM10 at the moment of sampling, continue and bring about changes in the isotope composition. This does not occur in the ambient air samples because in this case all chemical processes were finished before the sampling took place.

Figure 3 shows the carbon and nitrogen isotopic composition for the bulk measurement which was repeated in 2007. The results obtained for ambient air filters fitted to the area determined by the sources, although the most controversial samples, "Poly", were not measured because the small quantity was not sufficient for this extra analysis. The comparison of data measured in ambient air collected at "Indu", "Traffic" and "Zakopane" (Z10, Z11) site in 2006 (Fig. 1) and 2007 does not show big differences, the changes of nitrogen and carbon isotopic ratios are smaller than 1 ‰. However, the changes of nitrogen isotopic ratios measured in two "Zakopane", Z12 and Z9, samples were relatively high 1.5 and -4 ‰ respectively, (Table 1).

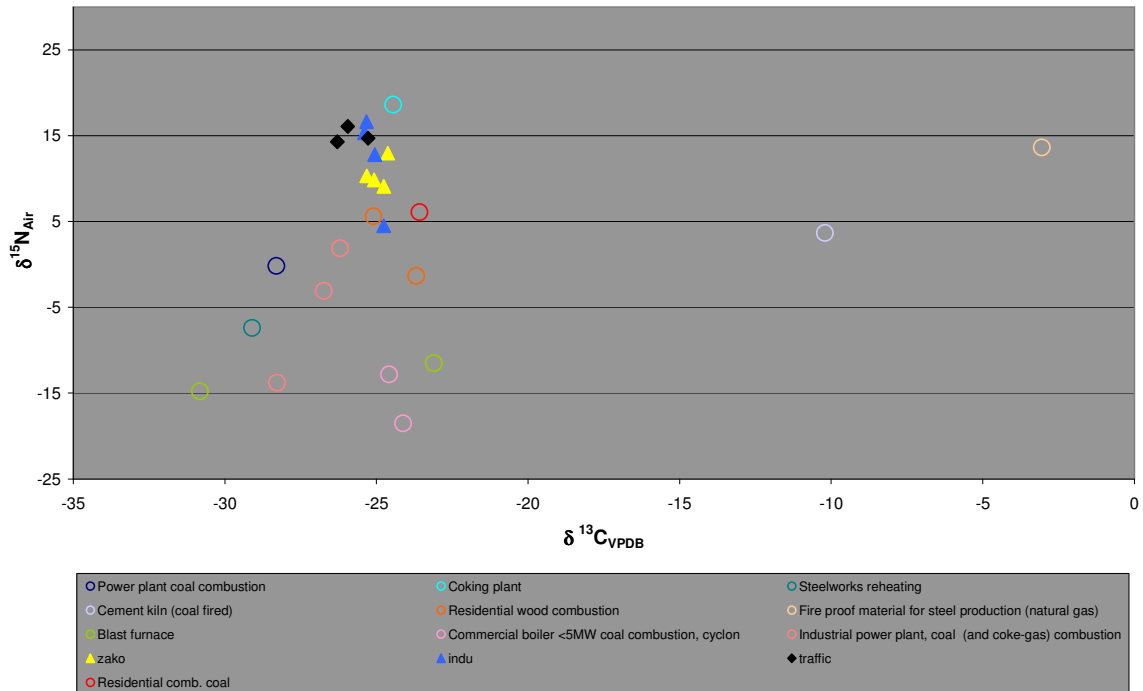


Figure 3. Carbon and nitrogen isotopic composition of the source and ambient air samples (Zako, Indu, Traffic) as analysed in July 2007.

Figure 4 shows the isotopic data obtained for the water-insoluble fraction of particulate matter, which contained a fraction of total aerosol organic nitrogen [16]. The water extraction removes inorganic ions containing nitrogen: nitrate, nitrite and ammonium and some organics containing nitrogen and carbon [4].

After water extraction all measured ambient air samples nicely fitted into the area represented by the sources. These data contain information which might be helpful for a source apportionment study but there are some difficulties. This experiment showed that the isotopic values of the source samples changed during one year of cooled storage leading to the problem with comparison of data measured before and after water extraction (water insoluble fraction).

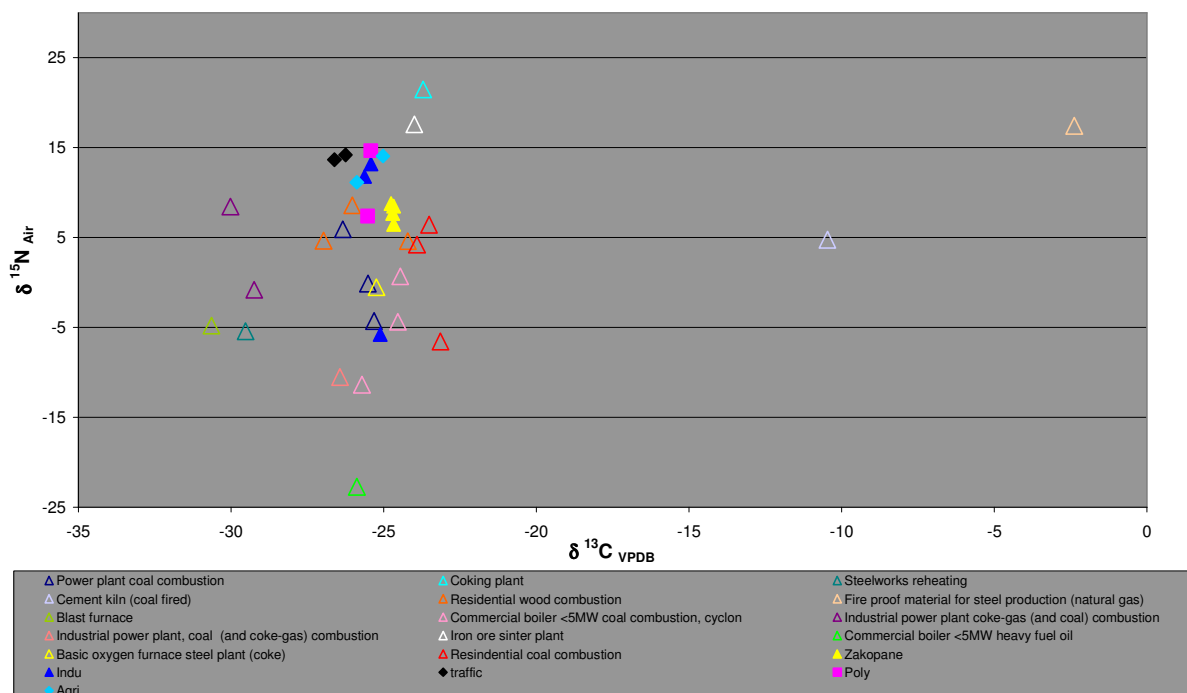


Figure 4. Carbon and nitrogen isotopic composition of water-insoluble particles in sources and ambient air samples (Zakopane, Poly, Agri, Indu, Traffic) measured in 2007.

If we establish that the changes in nitrogen isotopic composition (measured in 2006 and 2007) in the ambient air samples are negligible (smaller than 1 ‰), the water-insoluble fraction of Zakopane (Z10, Z11), Poly, Agri and Indu samples are lower in  $^{15}\text{N}$ . Traffic samples do not show this, but have the same  $\delta^{15}\text{N}_{\text{Air}}$  before and after water extraction.

In this study it is difficult to make a link between sources and ambient air samples after application of water extraction because of the problem with instability of isotopic compositions of the original source samples.

In future measurements, if necessary, the water extraction should immediately follow the bulk EA-IRMS measurement. Moreover, filter samples should be stored in a freezer at  $-20\text{ }^{\circ}\text{C}$ , to prevent the changes in isotopic composition.

## Conclusions

The isotopic data of particulate matter water-insoluble fraction may be helpful in a source apportionment study. Unfortunately, we can not use these data in our study because of the problem with instability of isotopic composition of source samples during storage.

In future measurements, the water extraction experiment has to immediately follow the bulk EA-IRMS measurement.

All filter samples should be stored in a freezer at -20 °C, to prevent the changes in isotopic composition.



Table 1. Carbon and nitrogen isotopic data (expressed in ‰  $\delta$  values) measured in all sources and air monitoring filter samples by EA-IRMS, estimated uncertainty for carbon and nitrogen was 0.25 and 0.4 ‰ respectively.

SOURCE TYPE		before water extraction				after water extraction	
		measured 04.2006		measured 07.2007		measured 07.2007	
		$\delta^{15}\text{N}_{\text{AIR}}$	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{15}\text{N}_{\text{AIR}}$	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{15}\text{N}_{\text{AIR}}$	$\delta^{13}\text{C}_{\text{VPDB}}$
Iron ore sinter plant	11Q1	23.47	-20.58	-	-	17.59	-24.00
Blast furnace	13Q1	-5.62	-20.50	-11.50	-23.11	-	-
	13Q2	-9.33	-23.42	-14.78	-30.83	-4.80	-30.64
Cement kiln (coal fired)	19Q2	2.45	-13.81	3.66	-10.21	4.75	-10.47
Power plant coal combustion	20Q1	5.38	-28.57	-0.18	-28.30	5.90	-26.34
	20Q2	-0.86	-28.57	-	-	-0.12	-25.52
	21Q1	0.12	-28.05	-	-	-4.28	-25.32
Industrial power plant coke-gas (and coal) combustion	12Q2	6.06	-25.43	-3.08	-26.74	-0.81	-29.24
	12Q1	7.03	-24.12	1.87	-26.20	8.44	-30.02
Fire proof material for steel production (natural gas)	18Q2	16.44	-4.69	13.64	-3.06	17.43	-2.38
Industrial power plant, coal (and coke-gas) combustion	14Q2	-14.08	-28.40	-13.77	-28.28	-10.52	-26.43
Basic oxygen furnace steel plant (coke)	15Q1	-1.72	-26.73	-	-	-0.53	-25.24
Commercial boiler <5MW coal combustion, cyclone	3Q1	-0.74	-18.46	-12.82	-24.59	0.68	-24.46
	4Q1	2.44	-18.57	-18.53	-24.12	-11.38	-25.71
	7Q1	4.70	-23.75	-	-	-4.38	-24.53
Commercial boiler <5MW heavy fuel oil	8Q2	-2.64	-26.66	-	-	-22.73	-25.88
Residential comb. coal	10Q1	6.61	-	6.08	-23.58	6.43	-23.52
	1Q1	8.00	-23.04	-	-	4.21	-23.91
	2Q1	3.19	-24.02	-	-	-6.57	-23.14
Residential wood combustion	5Q1	10.08	-25.05	5.60	-25.10	8.57	-26.03
	6Q1	-2.09	-26.70	-	-	4.65	-26.97
	9Q1	5.77	-23.66	-1.34	-23.69	4.59	-24.21
Coking plant	16Q1	20.36	-24.95	18.61	-24.45	21.46	-23.71
Steelworks reheating	17Q2	-7.47	-28.93	-7.40	-29.10	-5.44	-29.52

Zakopane	Z10	10.14	-24.37	10.31	-25.32	8.49	-24.68
	Z11	9.53	-25.06	9.84	-25.08	8.78	-24.76
	Z12	11.42	-24.43	12.97	-24.63	6.45	-24.68
	Z9	13.02	-24.15	9.11	-24.76	7.67	-24.71
Poly	H1R	9.46	-25.71	-	-	-	-
	H2R	23.18	-25.69	-	-	14.66	-25.42
	H3R	25.35	-25.50	-	-	7.39	-25.53
	H4R	19.86	-25.67	-	-	-	-
Agri	H16R	15.80	-25.20	-	-	14.06	-25.02
	H17R	20.67	-25.44	-	-	-	-
	H18	18.91	-25.66	-	-	11.14	-25.88
Indu	U3	4.68	-25.06	4.50	-24.76	-5.78	-25.12
	U6	16.47	-24.92	16.64	-25.33	13.19	-25.42
	U7	15.68	-24.53	15.33	-25.40	11.79	-25.63
	U9	13.57	-25.03	12.79	-25.06	-	-
Traffic	U4	13.78	-25.79	14.28	-26.29	13.65	-26.62
	U5	14.57	-25.60	14.70	-25.27	14.19	-26.25
	U10	15.17	-25.60	16.07	-25.95	-	-

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**Abstract**

Particulate matter samples were collected during two episodes of thermal inversion (14.01-2.3.2006) and at four different air monitoring stations in Krakow (Agri: urban background site, Indu: industrial site at Nowa Huta, Poly: domestic coal heating district, Traffic: traffic site) and from the Zakopane sub-urban mountain site (Zakopane), dominated by domestic coal heating. The carbon and nitrogen isotopic compositions of aerosol particles collected in the city of Krakow were measured in 2006 as part of the JRC-IES Krakow project, for which the samples were taken. A total of 42 samples (including 24 source samples) was analysed by Isotope Ratio Mass Spectrometry (IRMS) for isotopic ratios of N and C. The results for samples from different locations show clear grouping of related samples. The leftover of samples provided within the Krakow project were stored in the refrigerator. After one year of cool storage the EA-IRMS measurement was repeated and water extraction was applied. The aim of this experiment was to get more isotopic data for source apportionment. The results showed that the isotopic values of some source samples obtained in 2007 are different from these measured in 2006. However, these differences were not observed for ambient air samples. The possible explanation could be improper storage conditions causing continued reactions between products adsorbed on the filter during storage in the refrigerator.

The water extraction removed water soluble inorganic and organic nitrogen-containing compounds and caused the changes in  $\delta^{15}\text{N}_{\text{Air}}$ . In this study it is difficult to make a link between sources and ambient air samples after application of water extraction because of the problem with instability of isotopic compositions of the original source samples.

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